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Quarterly Progress
Report No. P-2236-10

PERMANENT MAGNET MATERIALS

April 1, 1953 to June 30, 1953

Prepared for
Chief of Naval Research, Department of the Navy
Under Contract No. Nonr-01002

Approved by:

Foster C. Nix

Foster C. Nix
Associate Director

Approved by:

Nicol H. Smith

Nicol H. Smith
Director

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| 7 | Dr. John Osborne
Material Engineering K-90
Westinghouse Electric Corp
East Pittsburgh, Penna. |

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ABSTRACT

A technique for preparation of fine Fe powders is described. The oxide produced by thermal decomposition of ferrous formate is reduced by hydrogen in the presence of calcium hydride. The evidence accumulated to date indicates that the ultimate particle size of the product is controlled by the temperature at which the ferrous formate is decomposed, rather than that at which the resulting oxide is reduced.

Some magnetic properties of the powders so produced are listed and discussed. A full interpretation of this magnetic data will be postponed, however, until a more complete range of powders becomes available.

1. INTRODUCTION

1.1 Purpose

More and more, relationships that exist between the structure of ferromagnetic materials and their magnetic behavior are coming to light. The purpose of this program is to study these relationships for permanent magnet materials. In particular, the relationship between coercive force and particle size in fine powders will be given special emphasis.

1.2 Scope

To investigate fundamental properties of permanent magnet materials.

2. PRESENT STATUS AND PROGRESS

2.1 Introduction

During the past quarter, the main effort of the project has been devoted to the development of the technique for preparation of Fe powders by reduction with CaH_2 . This technique was described briefly in Quarterly Progress Report P-2236-9. It will be discussed in detail here. A few studies of the magnetic properties of these powders have been made, and will also be discussed.

A melt with composition FeBe_2 was prepared, ground, and screened. Down to 325 mesh, no change in magnetic properties with screen size was observed. A further separation of the finest particles is needed.

2.2 CaH_2 Reduction Method for Preparing Fine Fe Powders

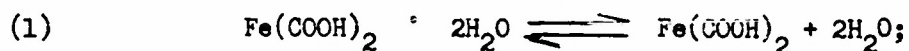
2.2.1 General Method

Iron powders are prepared by reducing an iron oxide whose

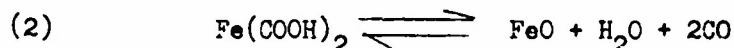
composition lies close to FeO, at temperatures from 175 to 300°C. The oxide is prepared by thermal decomposition of hydrated ferrous formate. Reduction is carried out under a controlled pressure of H₂. The water produced by the reaction is absorbed by CaH₂, which has been intimately mixed with the FeO powder. CaH₂ not only keeps the pressure of H₂O vapor at an infinitesimally small value, but also produces an extra molecule of H₂ for each molecule of FeO reduced to Fe. The quantity of H₂ produced can be used as a measure of the extent of reduction.

2.2.2 Preparation of Ferrous Oxide

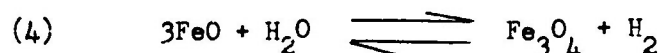
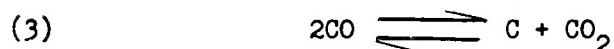
The ferrous formate is prepared by dissolving carbonyl iron in formic acid solution and precipitating the product under vacuum. This procedure was described in Quarterly Progress Report P-2236-6. The ferrous formate, in the form of small crystals of the dihydrate, is decomposed in a pyrex furnace chamber evacuated by a mechanical forepump. The decomposition is a two-step process - the first step occurs at about 100°C, and is apparently a loss of water of hydration



the second step occurs in the neighborhood of 300°C, although the exact temperature probably depends upon the rate of heating. This second step probably involves the thermal decomposition of the anhydrous ferrous formate:



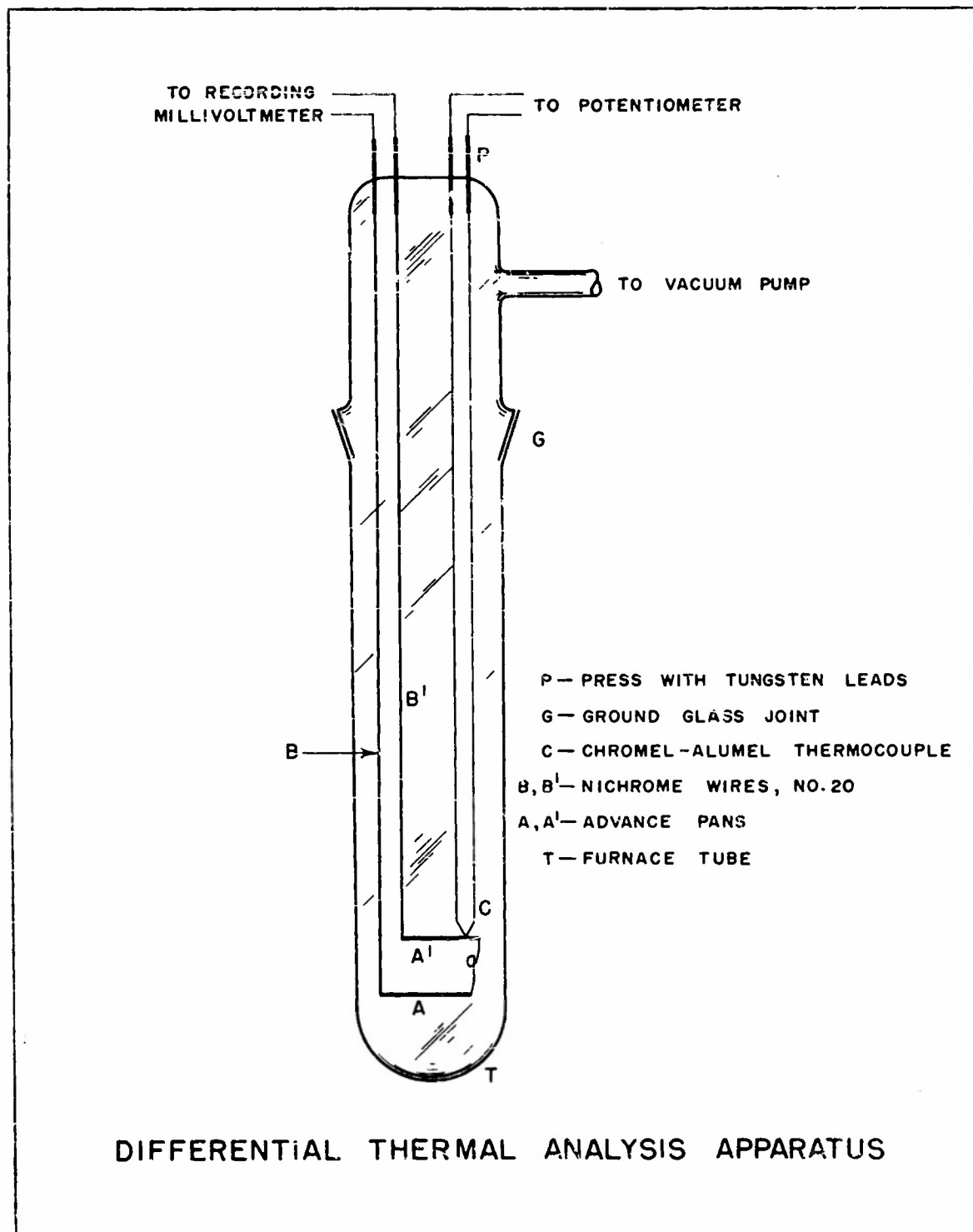
together with side reactions such as



occurring in the presence of the gaseous reaction products as they diffuse out of the powder mass.

The suggested reactions are hypothetical. In chemical analyses of the product, an insoluble black residue was noted when the sample was dissolved in sulfuric acid. This residue burned off on ignition. It was apparently carbon, and probably was produced by reaction (3) above. The total Fe content of the product in terms of FeO, amounted to 113% of the original sample. This indicates that the concentration of Fe in the product was higher than that corresponding to FeO, although the X-ray pattern of the product indicated no (< 1%) metallic Fe present. A complete analysis of this product has not yet been made, but the present chemical and X-ray data indicate that it is an homogeneous crystalline material with the same lattices as γ -Fe₂O₃ and Fe₃O₄, but with about 48 mole percent FeO and 52 mole percent Fe.

The temperatures at which the two steps occur were determined with a simple differential thermal analysis apparatus, of which a sketch is shown in Figure 2.1. A and A' are two small pans, about 1 cm x 1 cm, cut from thin sheet stock of Advance alloy. The pans are connected by Advance ribbon, and each is silver-soldered to a stiff nichrome wire support, (B and B'). The supports in turn are soldered to the tungsten leads in a press (P). A chromel-alumel thermocouple is also soldered to pan A' and brought out through the press. The ground joint (G) allows the furnace enclosure tube (T) to be removed for loading and cleaning the pans. The system is connected through suitable traps to a mechanical forepump, so that a pressure of less than 10 microns may be maintained.



About a gram of the sample to be analyzed is loaded into pan A', the furnace is assembled and pumped down, and then sufficient power is applied to the furnace to raise the temperature of the sample above any possible decomposition temperatures. The Advance pans plus the Ni-chrome supports form a differential thermocouple whose output is amplified and recorded. From time to time, the temperature of pan A' is measured with the chromel-alumel thermocouple or may be recorded if desired. When a reaction takes place in the sample, heat is either absorbed or evolved, and the temperatures of pans A and A' become different. The recorded trace of the differential thermal emf is normally a smooth curve, with peaks occurring where such a decomposition takes place, the direction of the peak indicating whether heat is evolved or absorbed.

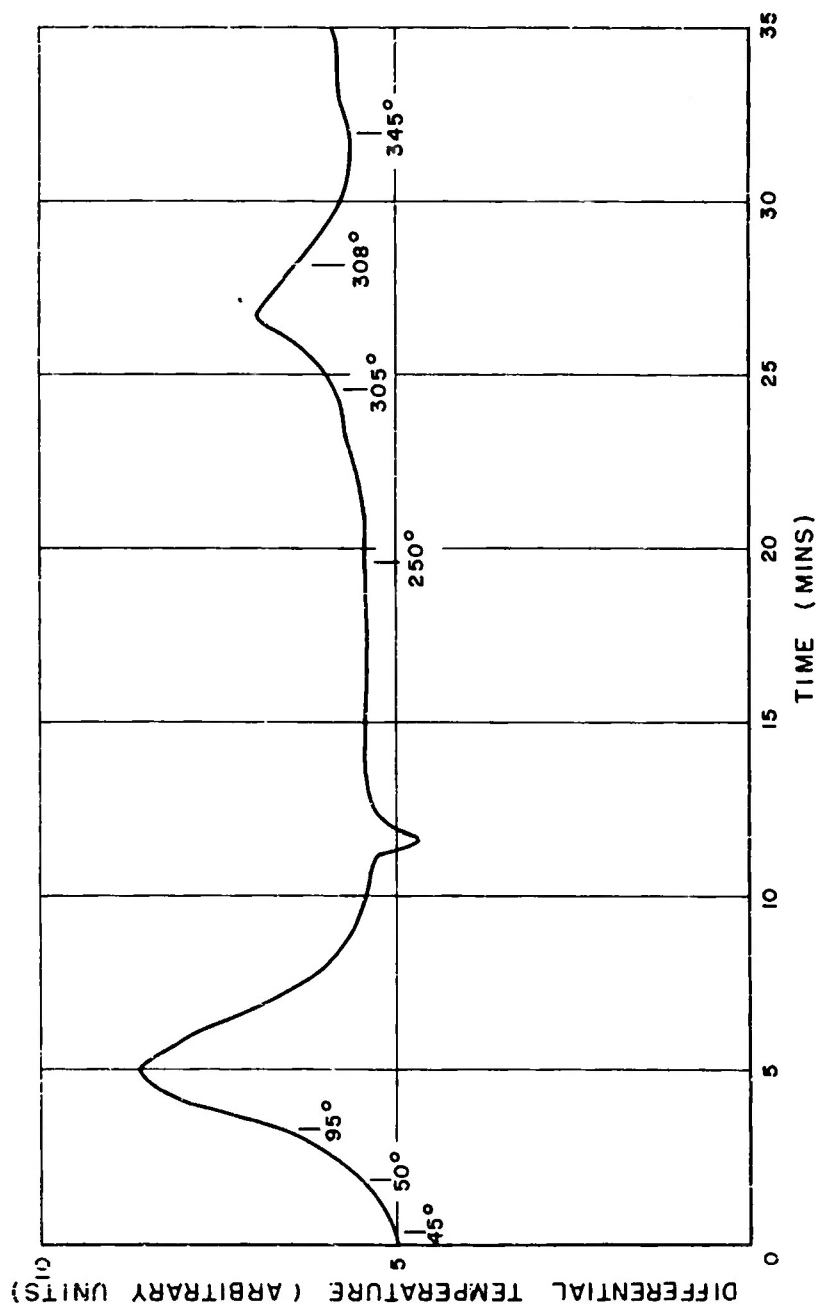
Figure 2.2 shows such a trace. The low-temperature peak, which is endothermic, is assumed to correspond to loss of water of hydration; the endothermic high-temperature peak to thermal decomposition of the anhydrous salt. The small exothermic peak always occurred, but has not been explored further. Occasionally the high temperature peak was exothermic rather than endothermic, which might be explained by a small leak in the system provided enough air was introduced to oxidize the FeO to Fe_3O_4 or Fe_2O_3 . A thermal analysis with this apparatus of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ showed peaks at 40-70° and 80-100°C. These agree with the data of Peltier and Duval⁽¹⁾, who attribute the first peak to loss of 1 1/2 moles of H_2O per mole of CaSO_4 , and the second to the remaining 1/2 mole of H_2O .

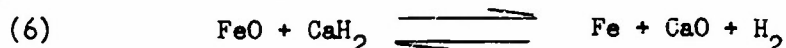
This decomposition is allowed to proceed for about 3 hrs. at 250°C. When the product has cooled, it is flooded with benzene to protect it from contact with the air.

2.2.3 Reduction of the Ferrous Oxide

The FeO powder is mixed with more than enough CaH_2 to allow for the reaction

RECORDER TRACE FROM DIFFERENTIAL THERMAL ANALYSIS





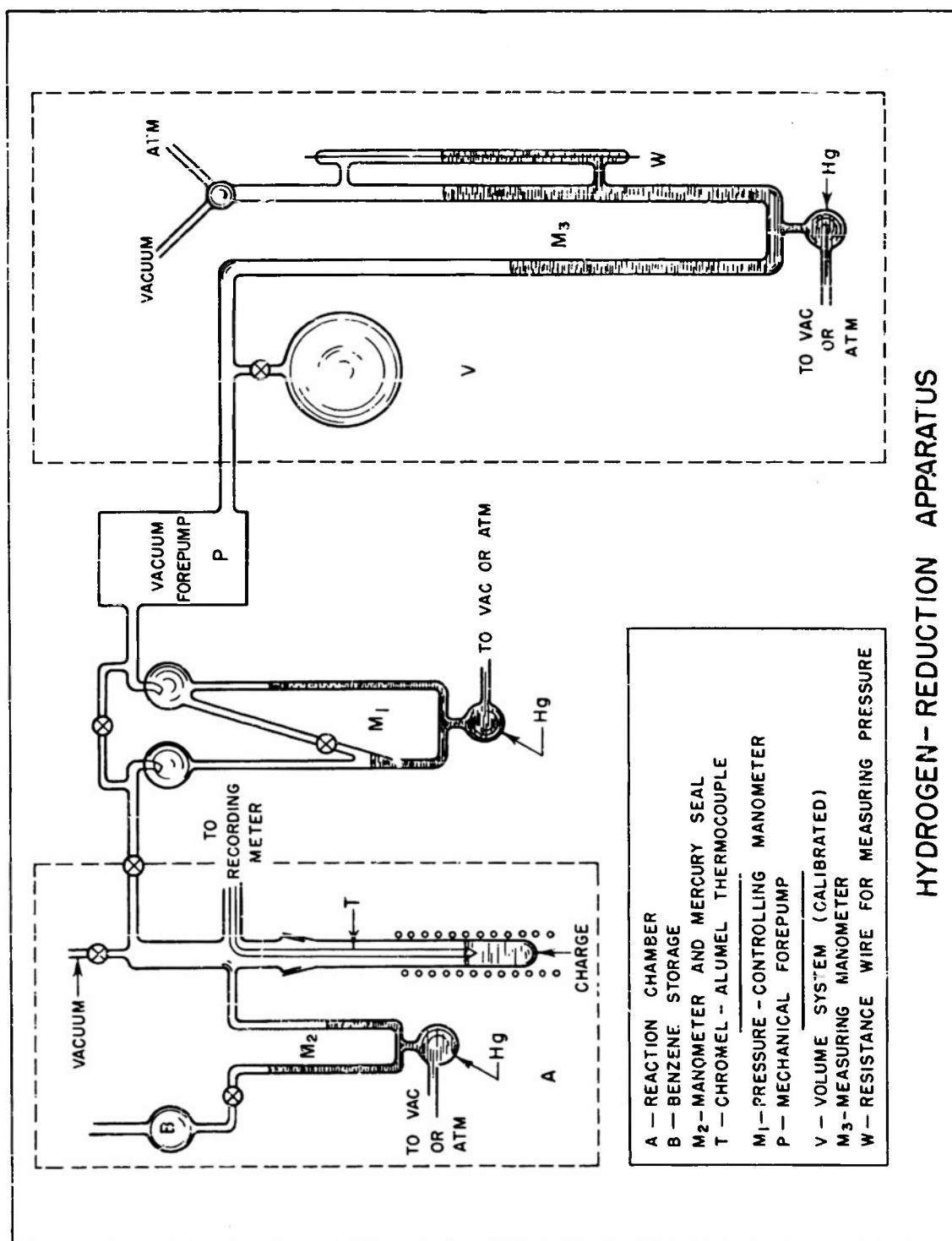
and with an inert filler powder, SiO_2 . The mixture is placed in a furnace chamber, the benzene pumped off, H_2 added to the desired pressure, and the furnace temperature raised to the appropriate value. The extra H_2 produced according to equation (6) is collected and measured in a separate chamber.

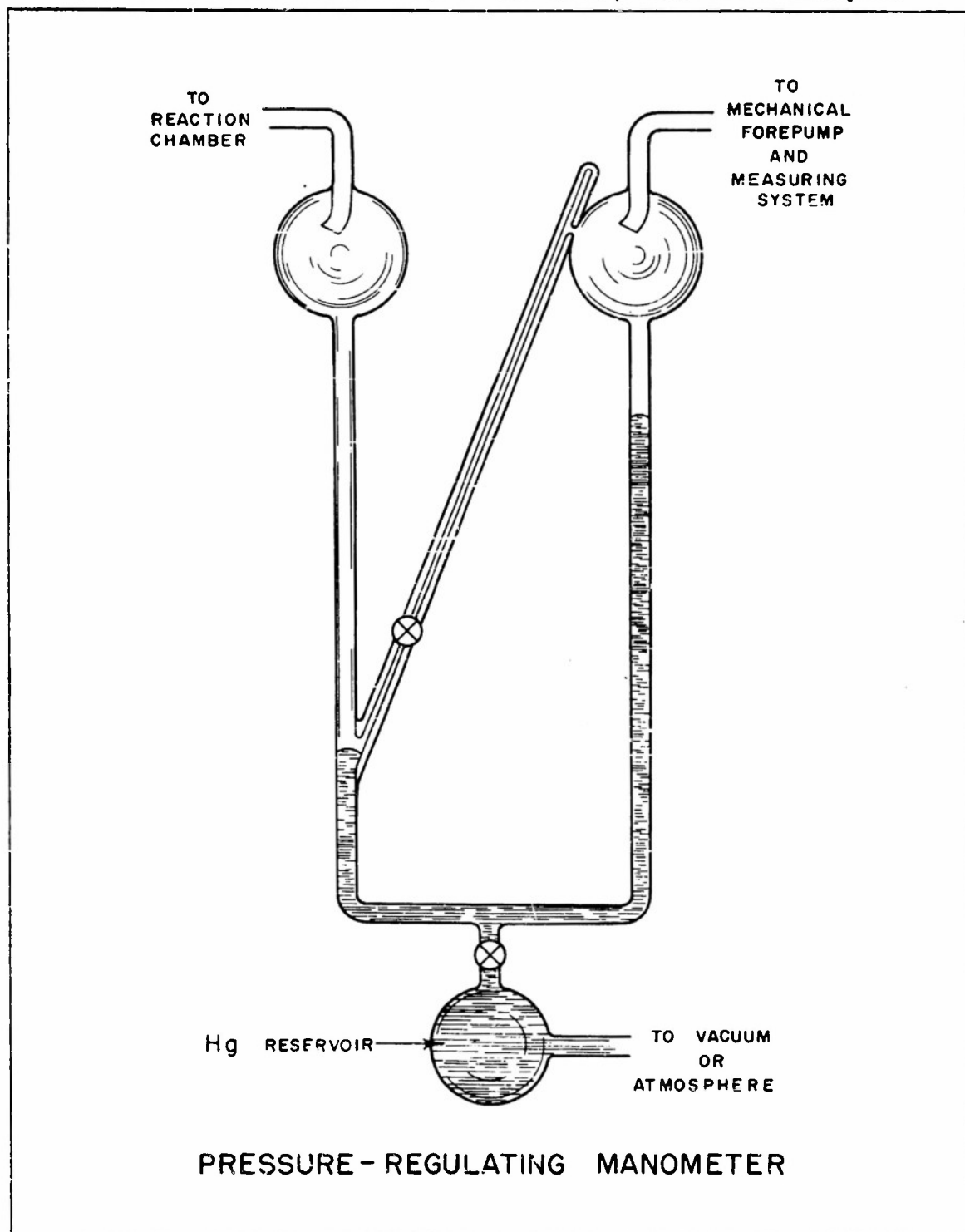
The apparatus used is shown schematically in Figure 2-3. It consists of two parts - the reaction chamber (A) and the measuring system (V) - connected by a "leaky" manometer (M) and a mechanical fore-pump (P). This manometer and pump transfer the excess H_2 from the reaction chamber to the measuring system, and maintain the H_2 pressure in the reaction chamber at a preset value. The manometer is shown in greater detail in Figure 2.4. Its construction is self-explanatory.

The reaction chamber of the reduction apparatus (Fig. 2.3) has a thermocouple (T) embedded in the reacting powder to measure its temperature and a benzene reservoir (B) to flood the product and protect it from the air after reaction is complete. A mercury trap (M_2) protects the reaction chamber against leaks around the stopcock (S_1). This trap also serves to measure the H_2 pressure during reaction.

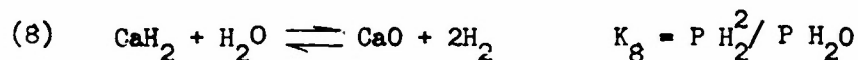
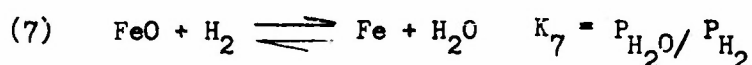
The measuring system is simply a known volume with a recording manometer (M_3). A nichrome wire (W) down the center of the manometer is one arm of a Wheatstone bridge. As the mercury in the manometer rises, the resistance of the wire is shorted out by the mercury column. The unbalance voltage of the bridge is amplified with a Liston-Folb d-c amplifier, and the amplified signal recorded on a 0-1 ma Esterline-Angus recording milliammeter. Since the volume (V) of the measuring system is known, this recorded pressure can serve as a measure of the extent of reaction (6).

The H_2 pressure during reaction was chosen to satisfy the





requirement that reaction (6) must proceed in the forward direction at a reasonable rate. The maximum allowable pressure required for the reaction may be calculated thermodynamically. The equilibrium constant of reaction (6) may be expressed in terms of those for the two reactions



Then for reaction (6)

$$(9) \quad K_6 = P_{\text{H}_2} = K_7 K_8$$

In Table 2.1 are listed values for K_7 taken from the data of Humphrey, King and Kelley(2); K_8 from Flood (3); and K_6 calculated according to equation (9).

Table 2.1 - Equilibrium Constants for Reduction of FeO by CaH₂

<u>T°K</u>	<u>T°C</u>	<u>K_7</u>	<u>K_8 atm.</u>	<u>$K_6 = P_{\text{H}_2}$ atm.</u>
298	25	9.6×10^{-4}	10^{41}	1×10^{38}
600	327	9.7×10^{-2}	10^{23}	1×10^{22}
800	527	2.4×10^{-1}	10^{19}	2×10^{18}

At any conceivable pressure whatsoever, the reaction (6) will proceed to the right.

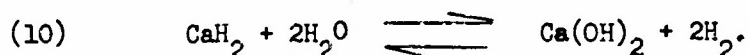
Experimentally, it is found that the reaction goes so readily that unless low H_2 pressures are used the temperature rise due to the heat of reaction becomes excessive, and the reaction velocity becomes regenerative. In this case, the entire reaction is over in five minutes or less, and a peak of undefined height occurs in the temperature-time

record. The particle size of the resulting iron powder is invariably greater than 350-400 Å when this temperature peak occurs.

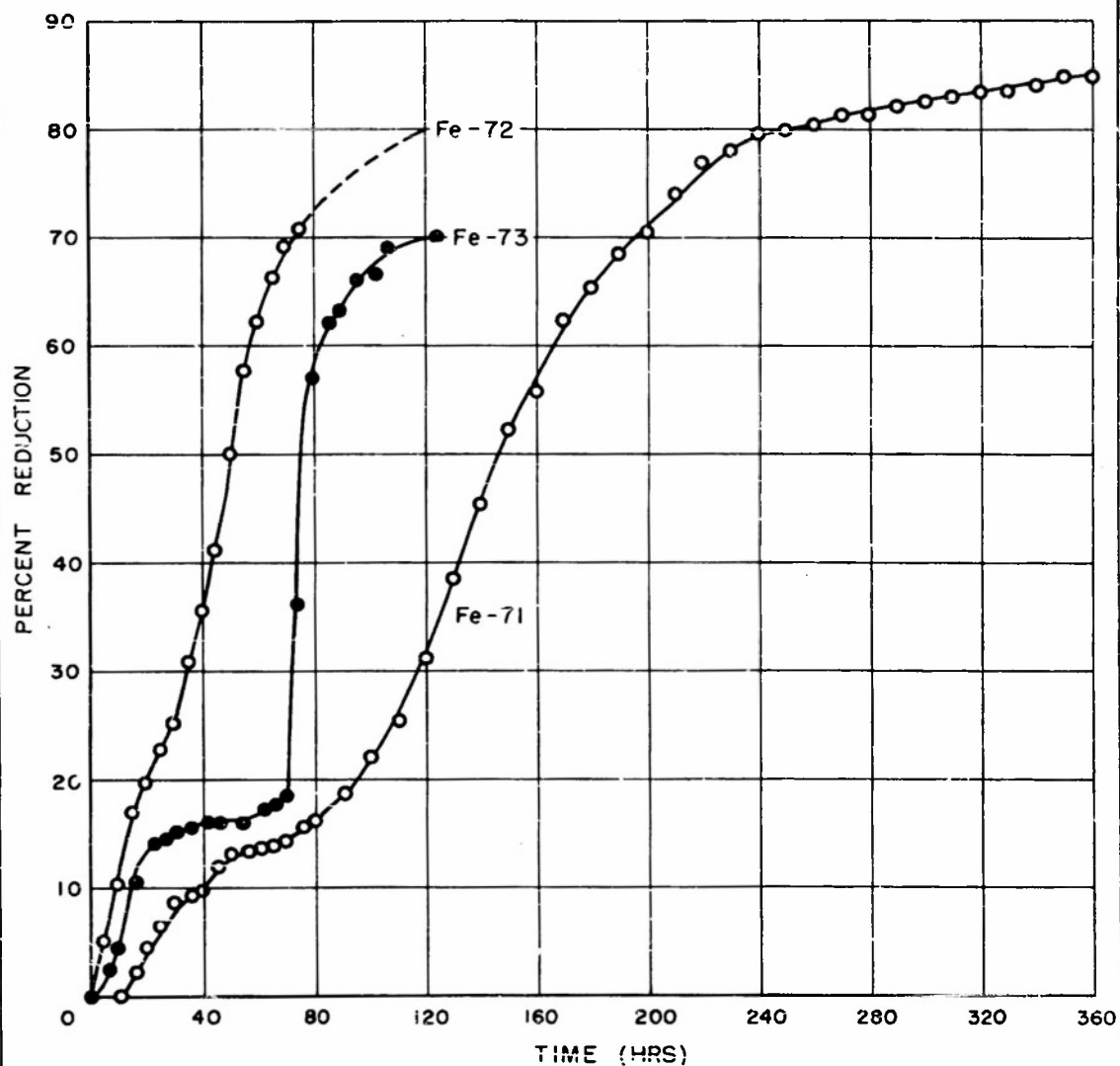
This effect is illustrated in Figure 2.5, which shows the course of reaction as a function of time for three identical samples of FeO formed by decomposition of ferrous formate at 255°C and reduced at 175°C. Figure 2.6 shows the temperature record for each of these runs. For Fe-71 and Fe-72, the H₂ pressure in the reaction chamber was kept at 6.5 cm of Hg, while for Fe-73 it was 10 cm. The FeO and CaH₂ powders were mixed by hand-grinding for Fe-71 and by ball-milling for Fe-72 and Fe-73. In both the Fe-71 and Fe-72 runs, the reaction was slow enough to maintain the temperature essentially at the control point. Ball-milling of the reactants before the run increased the reaction velocity somewhat. An increase in H₂ pressure from 6.5 to 10 cm of mercury increased the reaction velocity (after the initial portion) so much that a distinct peak occurred in the temperature record, as shown for run Fe-73 in Figure 2.6.

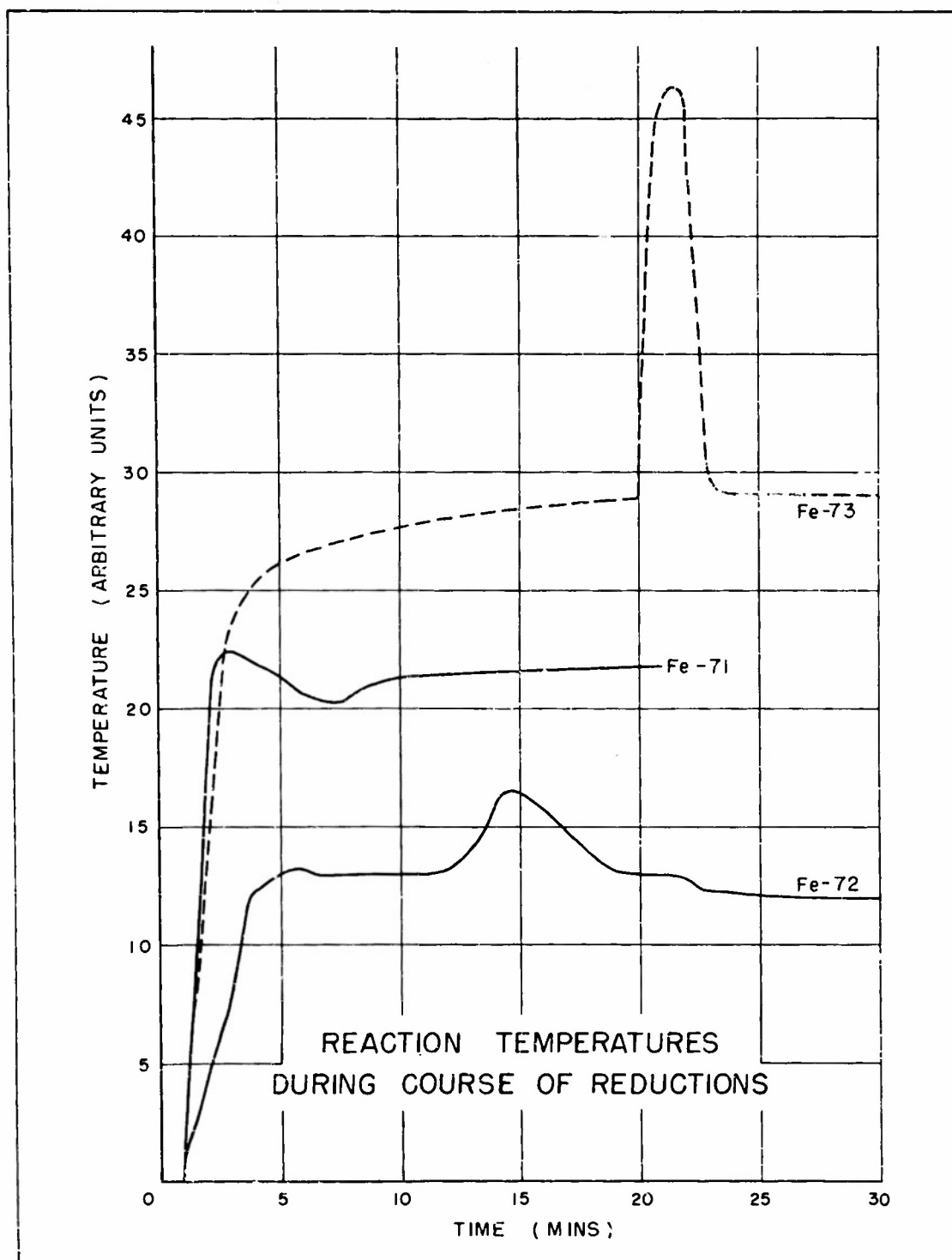
This tendency for the reaction to "take off" can be limited by keeping the H₂ pressure low, by incomplete mixing of the reactants, or by adding an inert (SiO₂) powder to the reactant mass. The tendency for "take-off" varies somewhat from one batch of ferrous formate to the next, and the measures taken to keep the reaction under control are set by experience with the first few runs of a new batch.

Several sources of uncertainty are present in correlating the amount of hydrogen evolved by the reaction with the extent of reduction. An uncertainty exists in the composition of the FeO. Furthermore, at low temperatures, CaH₂ reacts only partially with H₂O, ^(3,4) according to the equation



COURSE OF REDUCTION REACTION



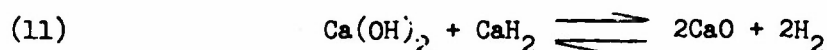


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FIGURE NO. 2-6

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Since according to this equation one H_2 is produced per H_2 used up in reducing the FeO , no net increase in H_2 pressure would occur. Flood⁽³⁾ has shown thermodynamically that at all temperatures the reaction should go all the way, as in equation (8). Below about $200^\circ C$, however, the low vapor pressure of H_2O over $Ca(OH)_2$ makes the second stage of the reaction



very slow. To test the completeness of reaction (11), excess $Ca(OH)_2$ was mixed with CaH_2 . The H_2 evolved at $300^\circ C$ accounted quantitatively for the CaH_2 present, indicating that under these conditions, reaction (11) goes to completion.

In practice, independent measurements of the overall extents of reduction are made by measuring the amount of H_2 evolved when approximately 100 mg of the product was dissolved in excess H_2SO_4 solution. Because of the appreciable solubility of H_2 in water solutions, only 2 cc of 5N acid are used, and the H_2 evolved is measured with mercury in a gas burette. Table 2.2 shows a correlation between the extents of reduction as measured by the reaction apparatus and by the acid dissolution method.

Table 2.2 - Comparison of Measurements of Extents of Reduction

<u>Powder</u>	<u>Acid Dissolution</u>	<u>Reaction Apparatus</u>
Fe-67	48	44
Fe-71	84	88
Fe-73	70	85
Fe-83	95	98
Fe-84	88	88

The agreement here indicates that measurement of the H_2 pressure during reaction is a useful way to follow the extent of reduction.

A typical reaction run under controlled conditions, as illustrated by Fe-71 in Figure 2.5, consists of three rather well defined portions. An induction period of 1-2 hrs. almost always occurs with FeO prepared at $255^\circ C$ and reduced under a H_2 pressure of 1-3 cm of mercury. Although occasional unaccountable variations occur in the length of this induction period, it appears to be insensitive to temperature or H_2 pressure. Following the induction period, a rapid reaction occurs, during which the extent of reduction increases from 15-20% to 70-80%. The rate of this portion appears to increase with increasing H_2 pressure. Finally, the reaction shows a slow tail, which is also apparently somewhat influenced by H_2 pressure.

In the technique of reduction as finally evolved, the FeO and CaH_2 are ground by hand for about two minutes under benzene. No inert material is added. Reduction is carried out initially under 2 cm of H_2 . When about 25% of the reaction is completed, the H_2 pressure is increased to an atmosphere and the reaction mixture is stirred by an a-c magnetic field whose amplitude is about 800 Oe rms. These conditions are used for FeO produced by decomposition of the formate at $255^\circ C$, and produce virtually complete reduction in about 8 hrs. For other decomposition temperatures, other conditions may have to be used.

2.2.4 Results

Table 2.3 lists the properties of some of the powders prepared during the course of the study of this system.

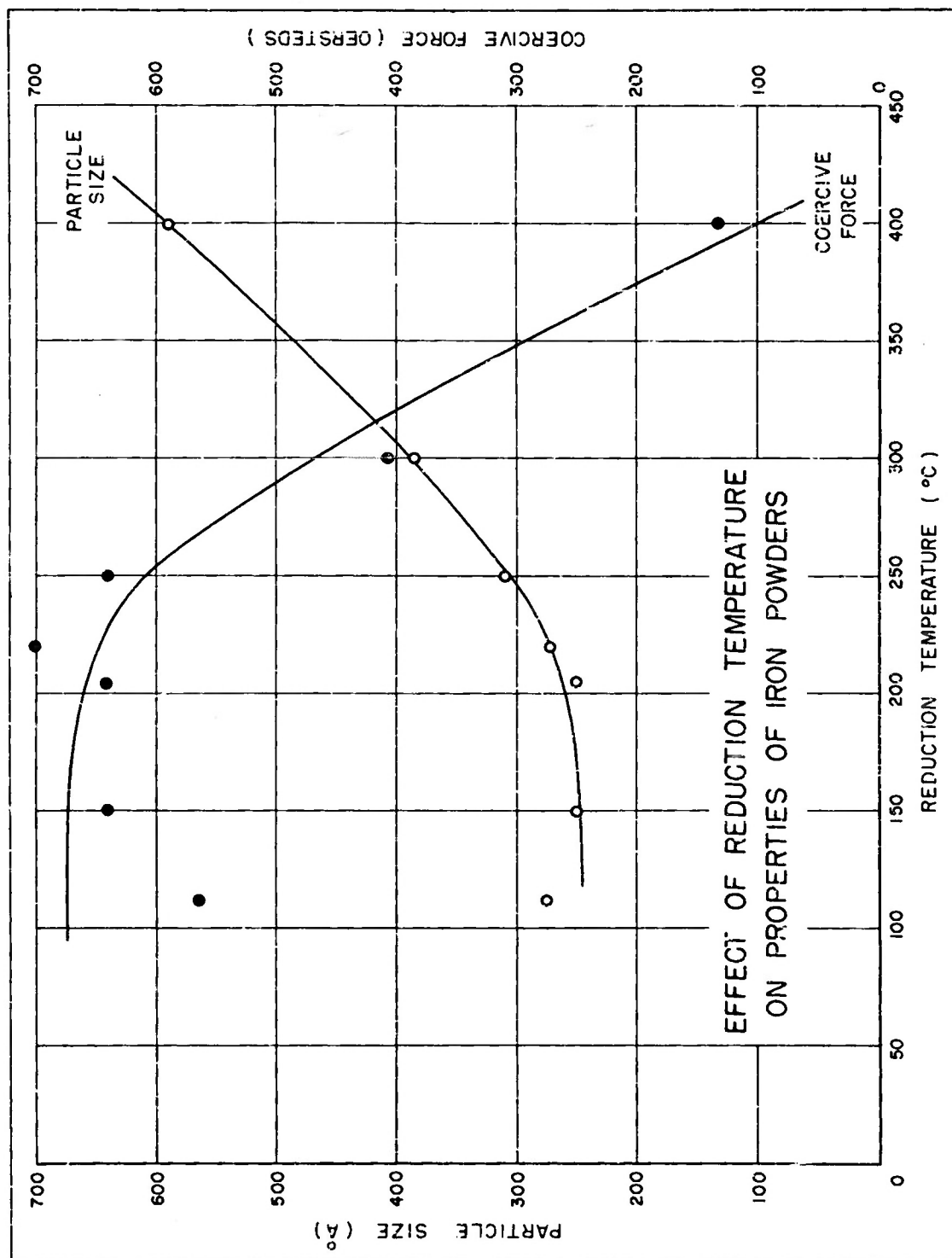
The first column lists the run number. The second column shows the reduction temperature. For all powders except Fe-85 (240°C) the ferrous formate was decomposed at 255°C. The percentage reductions in the third column are from acid-dissolution measurements. The simple Warren⁽⁵⁾ equation was used to estimate the particle sizes in the fourth column from the breadth of X-ray diffraction lines (see Quarterly Report P-2236-8 for details). The magnetic measurements listed in the fifth to eighth columns were made with the powders pressed lightly into glass tubes and measured with a Sanford-Bennett⁽⁶⁾ isthmus permeammeter. The measured coercive forces were converted roughly to infinite dilution using the equation⁽⁷⁾

$$(11) \quad (I_c^H) = \frac{(I_c^H)_{\text{measured}}}{(1 - v)}$$

$$(12) \quad v = \frac{4\pi I_s}{(\% \text{ Reduction}) (21400)}$$

where v is the volume fraction of the powder in the sample and 21,400 is roughly $4\pi I_s$ for pure Fe. Equation (11) assumes that only the metallic Fe makes any contribution to the saturation, which strictly speaking is not true.

Particle size and (I_c^H) values for the roughly-comparable powders 51 to 57 are plotted in Figure 2.7 against the temperature of reduction. For these powders, made from FeO decomposed at 255°C, there seems to be a lower limit in the particle size and an upper limit in the coercive force. For reduction temperatures above about 250°C, the increase in particle size may be due to sintering. The limiting particle size is probably controlled by the nature of the FeO. The effect of the temperature at which the ferrous formate is decomposed to FeO is illustrated by the comparison between the properties of Fe-81 and Fe-85. All conditions are identical save for this temperature, 255°C for



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FIGURE NO. 2-7

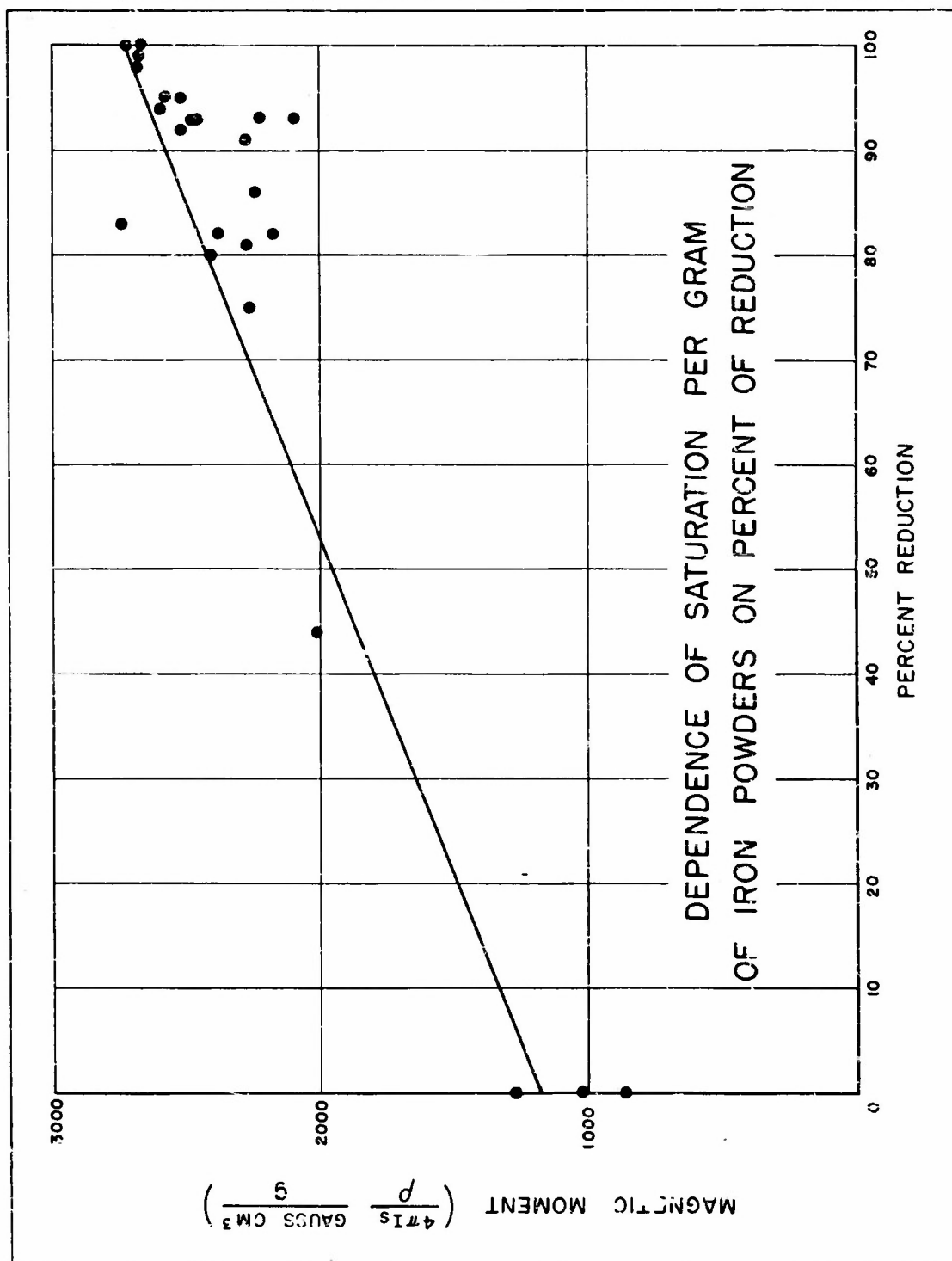
Fe-81, and 240°C for Fe-85. The particle size and coercive force values are 300 Å and 343 oersteds for Fe-81, and 200 Å and 935 oersteds for Fe-85. The coercive force roughly parallels the particle size, as found by Bertaut⁽⁸⁾. Work is now going on to try to distinguish the role played by the size of the FeO in the final particle size.

In the series of powders 66, 68, 69, 71, 81, 82, and 83, the particle size is roughly constant while the degree of reduction is varied. Data for these powders are gathered in Table 2.4.

Table 2.4 - Effect of Degree of Reduction
on Powder Properties

<u>Powder</u>	<u>% Redn.</u>	<u>$(I_c^H)_\infty$</u>
Fe-81	59	343
68	70	441
82	75	304
69	82	401
71	84	430
66	90	300
83	95	504

The coercive force does not seem to depend on the extent of reduction. On the other hand, the saturation magnetization does. In Figure 2.8, the magnetic moment per gram of the powders obtained by dividing the observed saturation by the weight of powder per cubic centimeter of sample, is plotted against the percent reduction. The straight line runs from the value of the moment per gram for Fe_3O_4 , 1180⁽⁸⁾, at no reduction, to the value for Fe, 2730, at 100% reduction. The large scatter is probably due to the uncertainty in measuring the weight



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FIGURE NO. 2-8

of powder alone in the sample. The fact that the points near 80-100% reduction lie below the line indicates that the residual oxide has a slightly lower moment than Fe_3O_4 .

Several of these powders were combined and pressed into small bars at various pressures up to 100 tsi by N. I. Ananthanarayanan at Lehigh University. Magnetic measurements were made on these bars in the isthmus permeammeter, and are summarized in Table 2.5

Table 2.5 - Magnetic Properties of Compressed Bars

Pressure tsi	$4\pi I_s$, gauss	$4\pi I_r$, gauss	(H_c) Oe	$(BH)_{max}$, ergs/cm ³
60	10,340	4850	260	4.1×10^5
80	9,370	4470	256	3.6×10^5
100	11,380	5610	245	4.5×10^5

The relatively low coercive forces indicate that the powders are larger than single domain. The values of $(BH)_{max}$ are too low to be of real value. This type of study will be repeated as powders in the single-domain range, similar to Fe-85, become available.

2.3

Conclusion

The study of the reduction process is beginning to bear fruit as the conditions necessary to produce single-domain powders with reasonably high degrees of reduction become clearer. The data presented here represent experimental powders produced as a by-product of the study of the reduction process. A more complete interpretation of the magnetic properties will be made when a more complete assortment of tailor-made powders becomes available.

3. FUTURE PLANS

The study of the reduction process will be continued during the next quarter. Particular attention will be paid to the role played by the temperature at which the ferrous formate is decomposed

to FeO. Curves of particle size and $(\frac{H}{C})_{\infty}$ against reduction temperature for various decomposition temperatures, similar to the one given in Figure 2.7, will be explored. The particle size and composition of the FeO will be studied as a function of this decomposition temperature.

Using the powders produced in this work, studies of the magnetic properties as a function of density in compressed compacts will be made. A series of compacts using Fe-85 at various volume fractions of powder has been prepared, and will be used to extent the approach to saturation work already begun and reported in Interim Report I-2236-2.

Work on a small scale on the FeBe₂ alloy powders already prepared will be continued. Ways of separating the smaller particles will be studied, and if they are successful, the magnetic properties as a function of particle size will be explored.

Alan D. Franklin

Alan D. Franklin
Project Leader

Since this investigation is still in progress, the conclusions expressed in this report are tentative.

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